TITLE: MECHANISTIC STUDIES AND DESIGN OF HIGHLY ACTIVE CUPRATE CATALYSTS FOR THE DIRECT DECOMPOSITION AND SELECTIVE REDUCTION OF NITRIC OXIDE AND HYDROCARBONS TO NITROGEN FOR ABATEMENT OF STACK EMISSIONS

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ABSTRACT

OBJECTIVE

The original objective of this project was to explore mechanistic aspects of the decomposition, oxidation, and selective reduction of nitric oxide (NO) over different cuprate catalysts, in order to design better catalysts for the NO_x control from both stationary and mobile power sources. Previous experiments had suggested that these cuprate catalyst candidates were promising.

In the meantime, however, we found that one of our newly developed and completely novel supported molten metal catalysts (SMMC), namely liquid indium supported on controlled porosity glass (abbreviated In-CPG-SMMC), provided superior catalytic activity and stability for the SCR of NO by ethanol, under net oxidizing conditions, in the presence and absence of water vapors, and at high gas hourly space velocities (GHSVs). It was, therefore, decided to instead pursue this even more attractive new catalyst for NO_x treatment.

SIGNIFICANCE OF PROJECT

Abatement of stack emissions from coal combustion is essential for the retention of clean air while utilizing the abundant coal reserves. Further, although lean burn or diesel engines are characterized by lower fuel consumption and CO_2 emissions than the current engines operating at a stoichiometric air/fuel ratio, the presence of oxygen in their emissions precludes the use of the current "three-way" type catalysts. The state-of-the-art

technology for NO removal from stationary sources involves the use of ammonia as the selective reductant with platinum, vanadium pentoxide, or zeolite containing catalysts, but this technique suffers from some limitations such as the maintenance of a sophisticated injector system, and the venting of any unreacted ammonia. For automobiles, use of nitrogen-based reductants is not viable, and the most promising technology so far is the use of hydrocarbon reductants with Cu-HZSM5 type catalysts. However, the activity of these catalysts drops significantly at higher temperatures and in the presence of water vapors, which are unavoidable in combustion exhausts. So, developing a commercially usable catalyst with good hydrothermal stability for NO abatement emissions from both motor vehicles and stationary sources is crucial.

ACCOMPLISHMENTS TO DATE

A flow-through reactor was adequately modified for NO related catalytic and adsorption measurements, including the on-line connection of a digital chemiluminescent NO-NO_x analyzer to the reactor outlet system.

Different molten metal catalysts were prepared, with indium loading varying from 0.95 w% to 28 w% (calculated amount for monolayer coverage). We tested the catalytic activity and selectivity of 28 w% In-CPG-SMMC for the SCR of NO, under net oxidizing conditions, at high GHSVs, at reaction temperatures from 350 to 550 ^{o}C, using a series of different reductants (H_2, CO, C_3H_8, C_3H_6, C_1-C_2 alcohols). Since ethanol was found to give the highest selectivity to N_2 (N_2O), we further tested the catalyst by comparing its activity and selectivity with those of HZSM-5 and In/γ-Al_2O_3, prepared by the impregnation method. At temperatures above 500 ^{o}C the ability of HZSM-5 and In/γ-Al_2O_3 to reduce NO to N_2 (N_2O) was surpassed by the supported molten indium catalyst. Generally water vapors have a slightly retarding effect on the conventional catalysts, but the presence of 10 % steam in the feed further enhanced the catalytic activity of In-CPG-SMMC over the entire temperature range studied. Using gas chromatography, besides CO_x and unreacted ethanol, we detected CH_3CHO, CH_4, CH_3CN, and traces of C_2H_4. Importantly, in the presence of water vapors the formation of the potentially harmful CH_3CN was completely inhibited. We also tested the limits of application of the indium catalyst by changing the GHSV, lowering the metal loading, and by varying the amount of reductant (ethanol) used.

PLANS FOR THE COMING YEAR

We next intend to further test the performance of our new catalyst at different catalyst loadings and under different conditions of oxygen, ethanol, and water content in feed. Further, we plan to explore some of the fundamental aspects related to the SCR process on this particular catalyst, including the reaction mechanism as well as the any catalyst deactivation. For this purpose, chemisorptive studies conducted on a TEOM® (Tapered Element Oscillating Microreactor)-microbalance as well as insitu infrared (IR) studies conducted on a Nicolet Magna-IR 560 type FTIR spectrometer will help us in understanding the nature of the catalyst and the mechanism of the reaction. This should aid in the further optimization of the catalyst and reaction conditions.

ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Journal Articles

- Halasz, I., Serban, M., Datta, R., “Efficient Reduction of Nitric Oxide by Alcohols in the Presence of Excess Oxygen and Water over a New Indium on Controlled Porosity Glass Supported Molten Metal Catalyst (In-CPG-SMC),” *Appl.Catal.B:Env*., submitted.

- Serban, M., Halasz, I., Datta, R., “New Water Tolerant Supported Molten Metal Catalysts (SMMC) for the Selective Reduction of Nitric Oxide by Ethanol,” *Catal.Today*, submitted.

Conference Presentations

- Serban, M., Halasz, I., Datta, R., “New Water Tolerant Supported Molten Metal Catalysts (SMMC) for the Selective Reduction of Nitric Oxide by Ethanol,” presented at *AIChE Conference*, Miami 1998.

- Serban, M., Halasz, I., Datta, R., “Selective Catalytic Reduction of NO by Ethanol over Indium Supported on Controlled Porosity Glass,” presented at the *New England Catalysis Society Conference*, Worcester 1999.

- Serban, M., Fishtik, I., Datta, R., “Kinetics and Mechanism of NO Selective Catalytic Reduction over Highly Active Novel Supported Molten Indium Catalyst,” presented at the *16th North American Meeting of the Catalysis Society Conference*, Boston 1999.

Students Supported under this Grant

- Manuela Serban, graduate (Ph.D.) student in chemical engineering, WPI.